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This is to notify you that the final report No. ARF-A216-7 entitled "Investigation of Narrow Line Paramagnetic Resonance Absorption Spectrum in Single Crystal Calcite" which was recently sent to you failed to have the following identification number RADC-TDR-63-69. We would appreciate it if you would put this identifying number in a conspicuous place in all copies you have received of this report and if you would please make reference to this identifying number when referring to this report.

Sincerely,

S. A. Marshall

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Solid State Physics

SAM:em

63-3-2

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NOTE: Effective June 1, 1963, the name of Armour Research Foundation of Illinois Institute of Technology will change to IIT RESEARCH INSTITUTE.

Report No. ARF-A1216-7
(Final Report)

INVESTIGATION OF NARROW LINE PARAMAGNETIC RESONANCE ABSORPTION SPECTRUM IN SINGLE CRYSTAL CALCITE

Rome Air Development Center

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

Report No. ARF-A1216-7
(Final Report)

INVESTIGATION OF NARROW LINE PARAMAGNETIC RESONANCE ABSORPTION SPECTRUM IN SINGLE CRYSTAL CALCITE

April 5, 1962, through November 5 , 1962

Contract No. AF 30(602)-2755
ARF Project A1216

Prepared by

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Attn: Mr. James Constantine - RAUAA

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FOREWORD

This is report No. 7 (Final Report) of ARF Project A216, Contract No. AF 30(602)-2755. This report covers the period 5 April, 1962, through 5 November, 1962. During this period work was performed on a program dealing with a five line paramagnetic resonance absorption spectrum produced in calcite single crystals by x-irradiation.

Personnel who contributed to this project include A. R. Reinberg and S. A. Marshall.

Data taken on this program are recorded in ARF Logbooks C12422, C12812 and C12813.

Respectfully submitted,

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ABSTRACT

INVESTIGATION OF NARROW LINE PARAMAGNETIC RESONANCE ABSORPTION SPECTRUM IN SINGLE CRYSTAL CALCITE

The results of a program of study are presented on the Investigation of a Narrow Five Line Spectrum in Irradiated Calcite Single Crystals. The objective of the program was to discover, by a systematic investigation of the properties of the electron paramagnetic resonance absorption spectrum of these five narrow lines, the defect center or centers responsible for the spectrum. A secondary objective of the study was to make recommendations regarding the usefulness of this spectrum for a quantum-electronic device. To date, we have concluded that this five line spectrum is generated by more than one defect center. The conclusion was reached by comparing the irradiated and unirradiated spectra. We have also discovered the spectrum of what we tentatively call a "butterscotch" defect center. This defect center appears to be a CO_2^- ion located at a carbonate ion site in calcite.

INVESTIGATION OF NARROW LINE PARAMAGNETIC RESONANCE ABSORPTION SPECTRUM IN SINGLE CRYSTAL CALCITE

I. INTRODUCTION

One of the most intensively studied crystal-ion systems in electron paramagnetic resonance absorption spectroscopy has been divalent manganese in calcite.[1-5] The intensity of this interest, even though only one ion in this structure has to date been studied, is due to at least three fundamental reasons. The first and perhaps most important reason is the S-state character of the divalent manganese ion. Ions having an S-state or a state of zero orbital angular momentum have been the object of much interest because of the uncertainties in the mechanisms which give rise to the splittings of the six-fold degenerate spin state.[6-18] A second reason for the interest shown in these ions is the finite hyperfine structure observed in its resonance absorption spectrum. If divalent manganese were truly an S-state ion composed of an outer shell of five 3-d electrons, the spectrum would exhibit no hyperfine structure since d-electrons have zero probability of being at the manganese nucleus. The true wave function of this ion can thus be concluded to consist of an admixture of functions which yield nonvanishing amplitudes at the manganese nucleus. The exact nature of this admixture has been studied by many investigators for reasons bearing on such subjects as magnetic resonance absorption spectroscopy, electron nucleus double resonance absorption spectroscopy and interactions giving rise to ferromagnetism. The third reason for the interest shown in this system and the reason most closely associated with our interests arises from the fact that in calcite, the most abundant nuclear species of calcium, carbon and oxygen have zero spin quantum numbers. To be specific, carbon-14 has an abundance of 97.1%. Because of this very high percentage of zero spin nuclei in the calcite, one would expect the widths of magnetic resonance absorption lines to be comparatively narrow as a result of negligible nuclear hyperfine interactions. Furthermore, since divalent manganese has zero orbital angular momentum, one would expect the widths of the resonance absorption lines to be narrow compared to line widths of non-S-state ions because of the reduced spin-orbit interaction. This interaction couples the electronic spin system to the lattice via the gyrating motion of an orbiting electron. With this coupling, the lattice can, so to speak, interupt the state of a spin causing a lifetime broadening of the resonance absorption lines.

It is for two of these reasons that a strong interest should naturally be aroused in the study of irradiation produced defects in calcite.[19-21] The two reasons alluded to here are the zero spin character of the calcite structure nuclei and the fact that in general, irradiation-produced species tend to have either S or sigma state characters. The measurements made to date in this program reveal the existence of a spectrum of at least five narrow lines. It is our opinion that the narrowness of the five line spectrum is due in part to the S or sigma state character of the paramagnetic species responsible for the spectrum and in part due to the lack of hyperfine and super-hyperfine structure.

II. TECHNICAL DISCUSSION

The objectives of this program of research have been clearly stated to be a) identification of the species responsible for the five line paramagnetic resonance absorption spectrum and b) to provide an estimate of the potential usefulness of these absorptions for a quantum-electronic device. With these objectives in mind, we have undertaken a program of activity to study the complete paramagnetic resonance absorption spectrum of unirradiated and irradiated clear and "butterscotch" calcite. As a companion effort to the magnetic spectrum of these calcite specimens we have also undertaken an investigation of their optical resonance absorptions ranging from 2.8 microns wavelengths to 2000 Angstroms wavelength.[22] In order not to unduly complicate the analysis, we have arbitrarily decided to use only x-irradiation for the first phase of this program. Only after those defects specifically generated by x-rays have been identified would it be scientifically prudent to go to such sources of radiation as neutrons, electrons, or gamma rays since such radiations cause in addition to energetic electrons such catastrophic events as knock-on collisions and displacements, fractures, production of radioactive species, etc.

As an initial phase to this program we have undertaken a complete mapping of the optical and magnetic spectra of calcite. Between 2000 Angstroms and 2.8 microns wavelength, the optical spectrum of unirradiated clear and "butterscotch" calcite presents no complexities. Clear calcite has of course been studied in detail during the period of the early 1930's. At

2100 Angstroms, clear calcite exhibits a sharp cut-off in its transmission which is due to the fact that the crystal behaves as a beyond cut-off transmission line. Near 1.8 microns the clear calcite exhibits a number of complex absorption bands which have been explained as being due to vibrations of the various modes of the carbonate ion. Butterscotch calcite of course exhibits exactly the same long wavelength absorption bands as those exhibited by clear calcite. The only difference in the optical absorption spectra of the two kinds of calcite occurs at the short wavelength cut-off which occurs near 2500 Angstroms for "butterscotch" calcite. Figure 1 shows the spectra for clear and "butterscotch" calcite in the visible and near ultraviolet region.

The electron paramagnetic resonance absorption spectra of both clear and "butterscotch" calcite are, except for one set of three absorption lines, nearly identical. This one exception of three lines is referred to as the "butterscotch" spectrum about which more will be said presently. Using an x-band electron paramagnetic resonance spectrometer with superhetero dyne detection and with the specimen held at 77°K we have observed a total of 120 absorptions in the field region from zero to 10,000 oersteds. This spectrum was observed with the specimen so oriented as to have the Zeeman field vector parallel to the crystal [111] direction (see Figs. 2a and 2b). The reason for exploring with the crystal so oriented is to provide a spectrum which exhibits a minimum complexity. When the crystal is not so oriented the total number of lines is observed to increase markedly, the exact

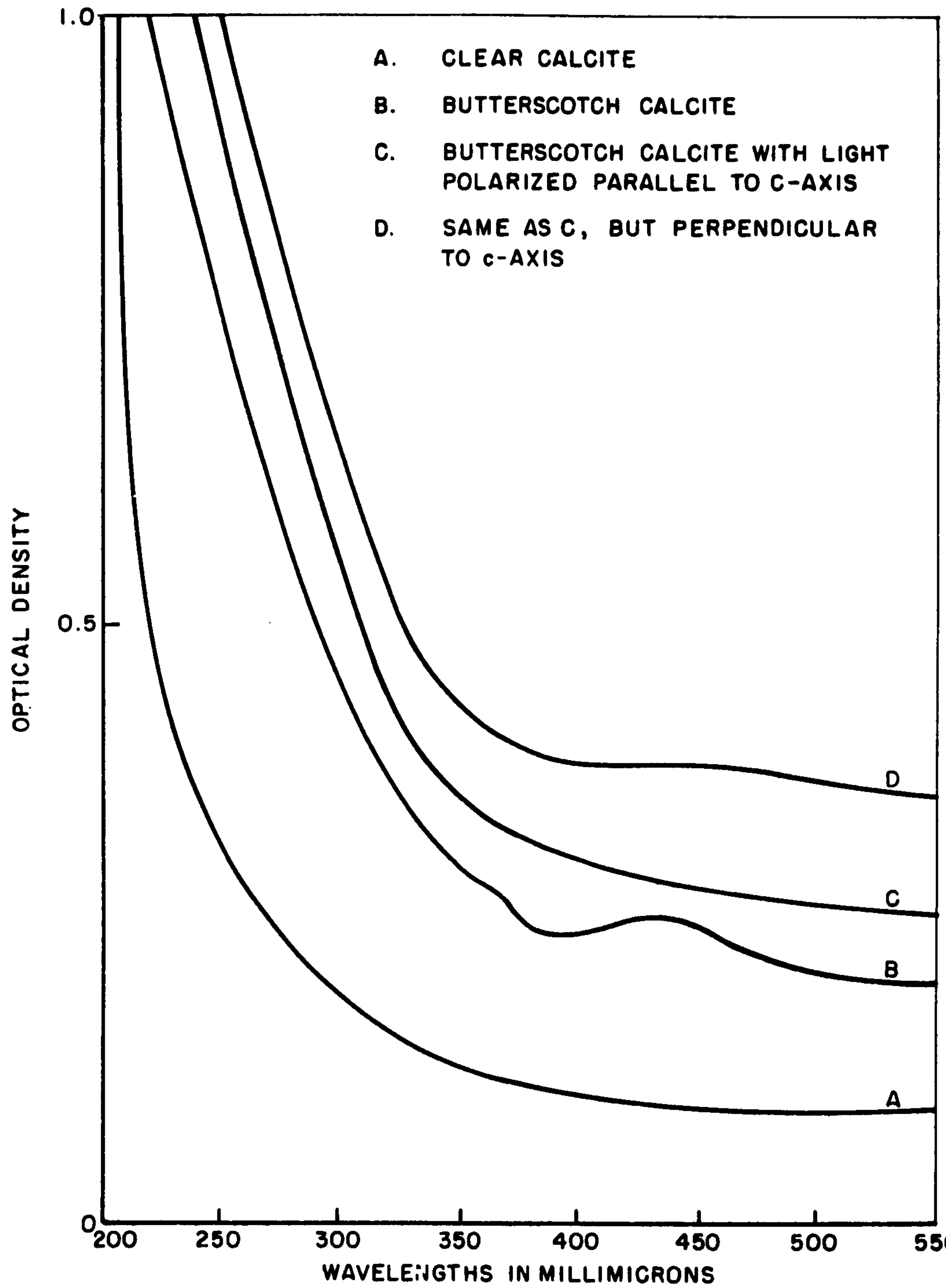

Figure 1. Optical Absorption in Calcite

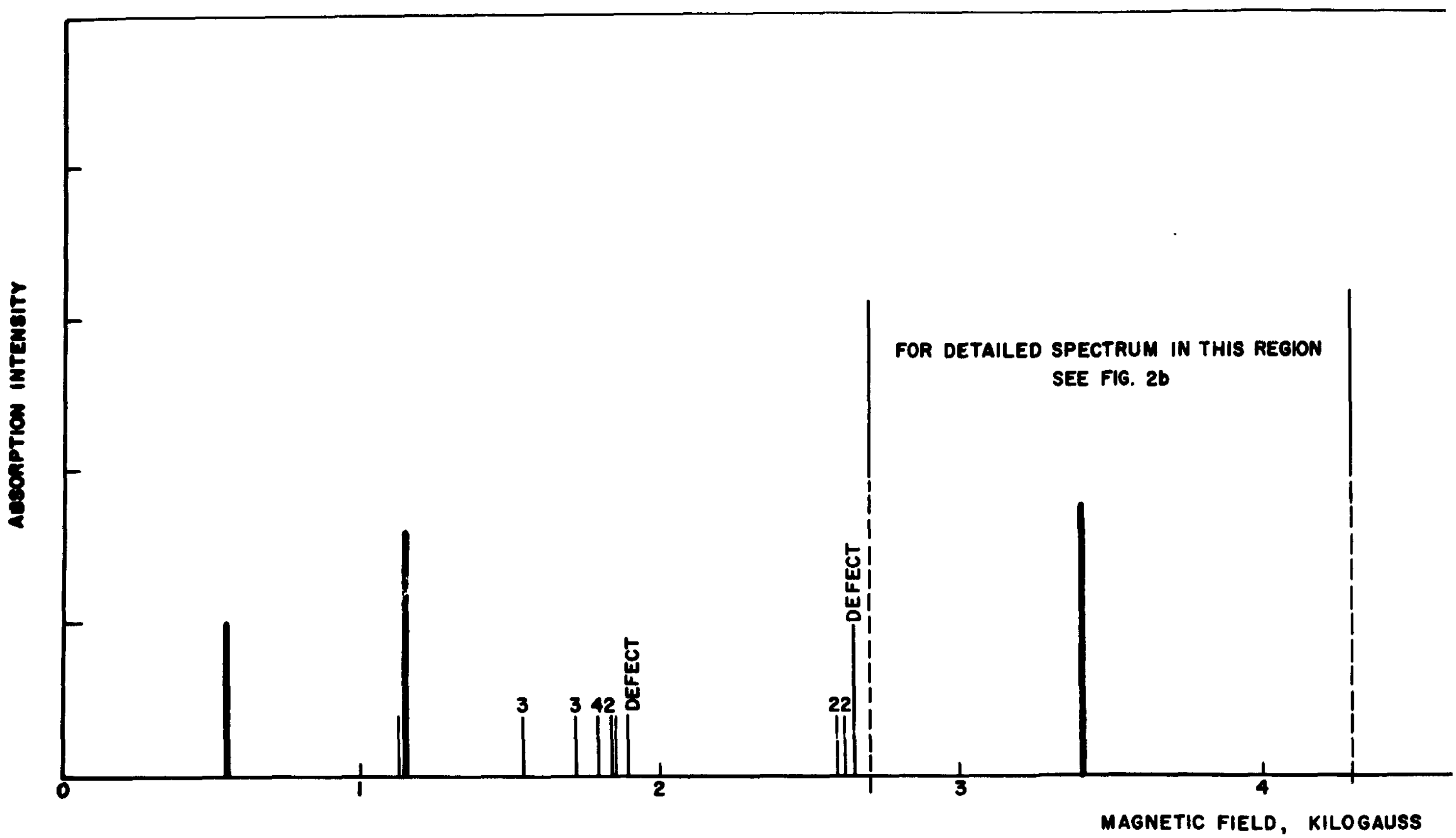

FIG. 2a OBSERVED MAGNETIC RESONANCE ABSORPTIONS

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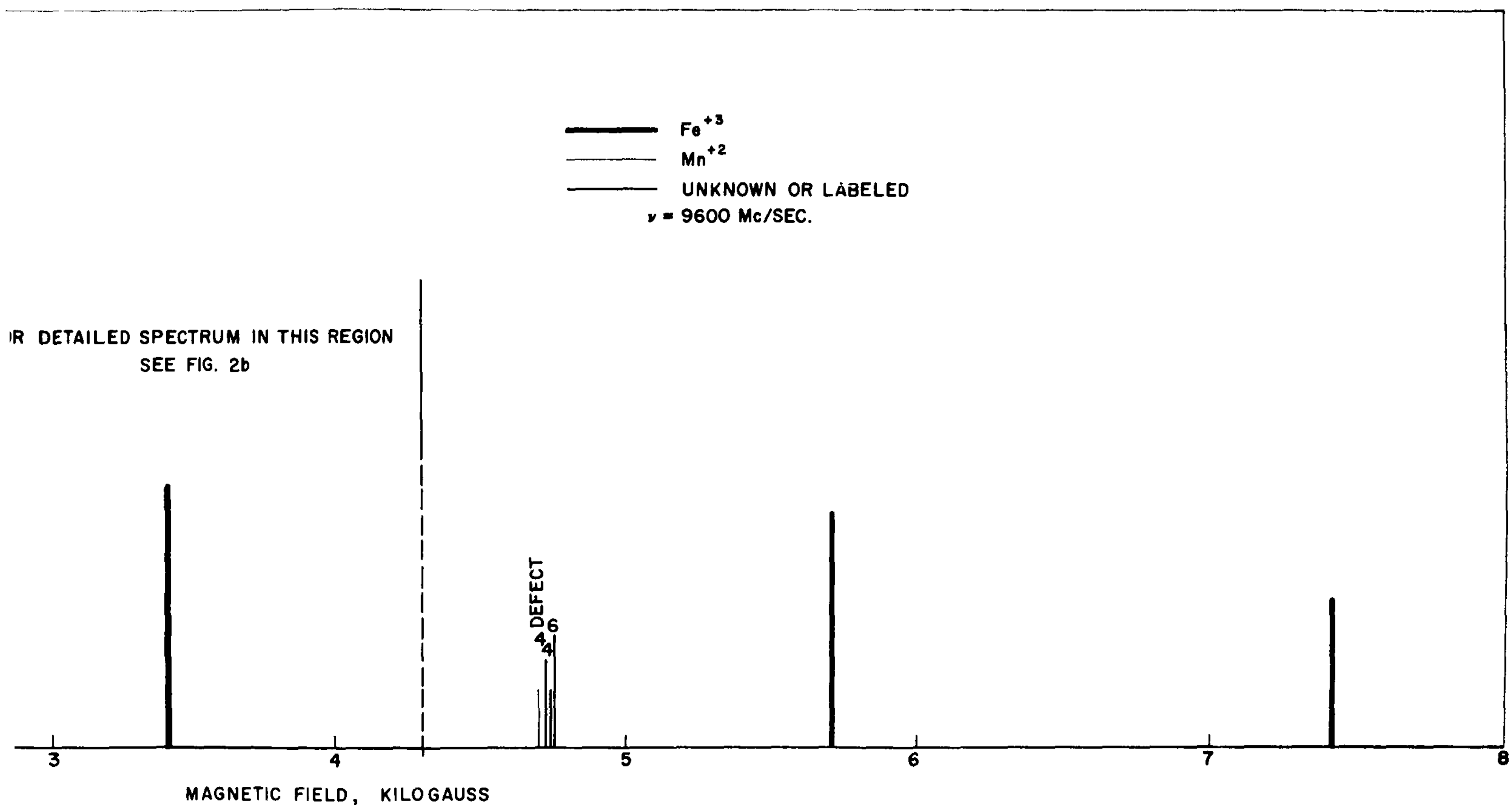

MAGNETIC RESONANCE ABSORPTIONS IN SINGLE CRYSTAL CALCITE

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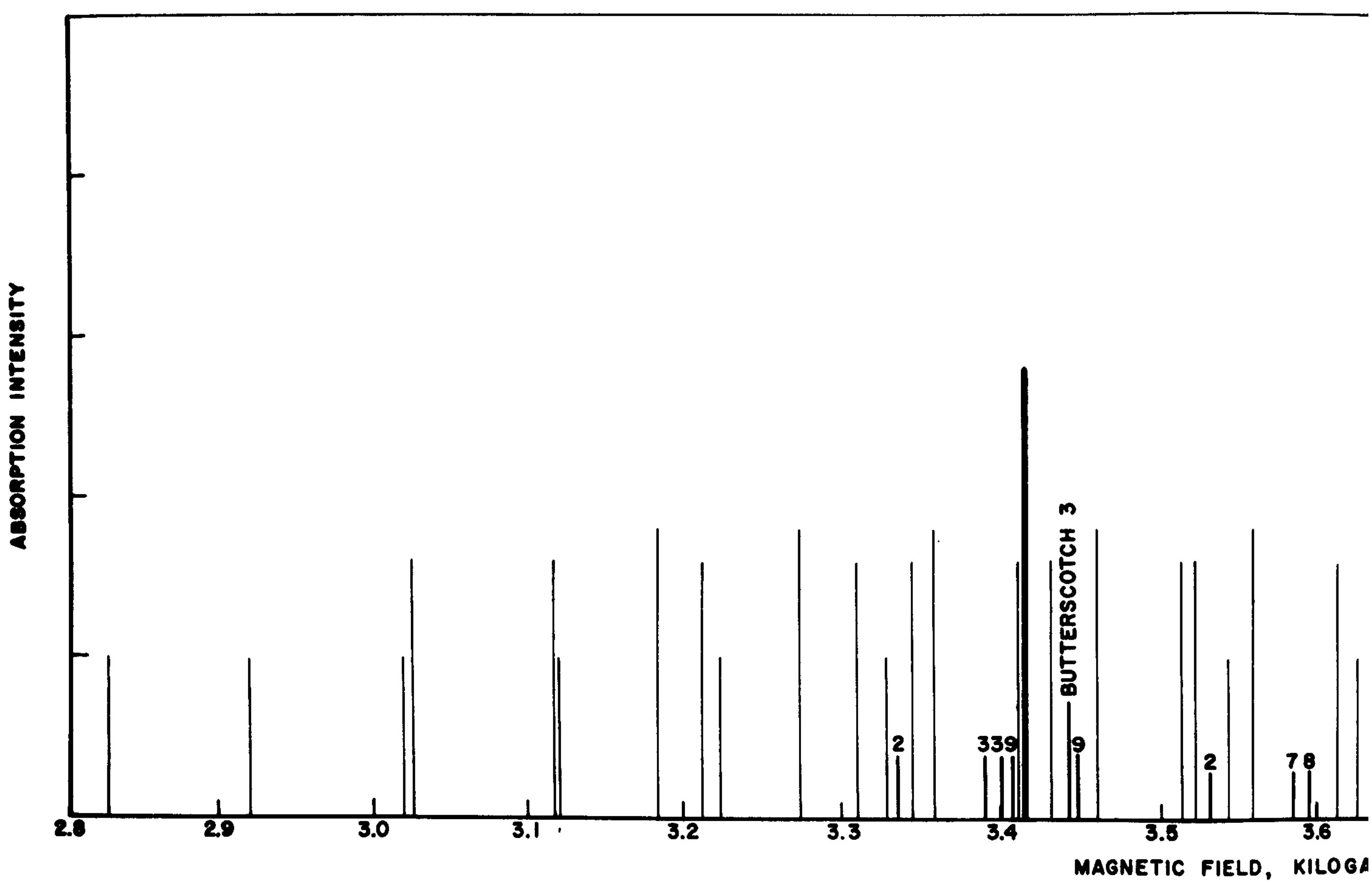
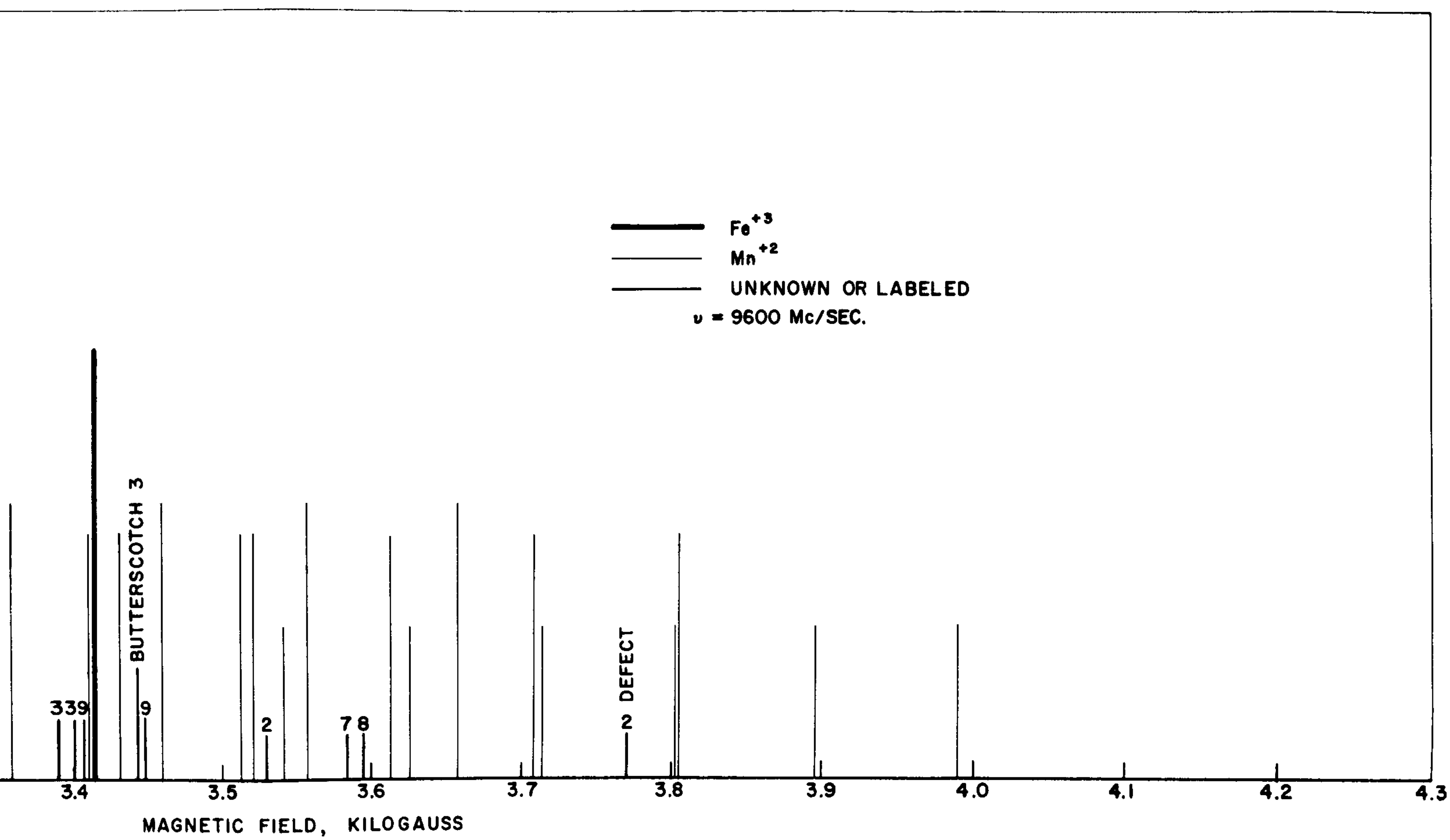


FIG. 2b OBSERVED MAGNETIC RESONANCE ABSORPTION



ETIC RESONANCE ABSORPTIONS IN SINGLE CRYSTAL CALCITE

CH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY number being difficult to determine because of crowding and superposition of lines in the region of 3400 oersteds.

Of the 120 lines catalogued when the Zeeman field is oriented parallel to the crystal $[111]$ direction, we have been able to identify the following:

a) Thirty lines due to divalent manganese

b) Five lines due to trivalent iron

c) Three lines due to the "butterscotch" defect

d) Four lines which are identical to four of the five lines found in irradiated calcite.

The remaining 78 lines observed in the unirradiated calcite remain as unknown quantities for the present and unless there occurs a change in the objectives of the program they will not be studied.

At this point a brief explanation will be given of this set of identified spectra. In the case of divalent manganese, we have as stated previously, an ion whose ground electronic state is nondegenerate in orbital angular momentum and six-fold degenerate in spin angular momentum. This six-fold degeneracy is removed by the axially symmetric crystalline electric field generated by the six-fold coordinated carbonate octahedron. (We have assumed here that the divalent manganese ion occupies a calcium ion site.) The system of ion and crystal now has three energy states, each being two-fold degenerate in spin and labeled as $S = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$. Application of a magnetic field removes this two-fold degeneracy yielding six non-degenerate states. Between these six states we can have five so-called fine structure transitions and since the manganese nucleus has a spin state of 5/2 we have a total of 30 resonance absorption lines.[1]

The case of trivalent iron is precisely the same except that the most abundant nuclear species of iron has zero spin so that the spectrum consists of five fine structure lines. We have analyzed this spectrum in some detail (although not in this program) and have arrived at those spin-Hamiltonian constants which predict all five fine structure line magnetic field positions to a precision of one part in 3000 (see Table I).

The three line spectrum observed in "butterscotch" calcite has also been observed in clear calcite but at a greatly reduced intensity. With the Zeeman field vector oriented parallel to the crystal [111] direction this spectrum collapses into one line. Rotating the Zeeman field vector away from this direction but in a plane of constant azimuthal angle φ produces a spectrum of three lines which collapse into two or three lines at $\Theta = 90°$, depending upon whether φ is or is not a multiple of 30°. If the Zeeman field is not rotated in a plane perpendicular to the crystal [111] direction, a spectrum of two or three lines is observed depending upon the direction of the Zeeman field vector. We have noted that when this perpendicular spectrum consists of three lines they are of equal intensity and when it consists of two lines, one of the components is twice the intensity of the other. We have also noted that this perpendicular spectrum exhibits a three-fold rotational symmetry about the crystal [111] direction. From the directional characteristics of this "butterscotch" spectrum we have concluded that the paramagnetic

TABLE I

Spin Hamiltonian and constants for Fe^{+3}-calcite spectrum evaluated at 77°K.

$$\mathcal{H} = \beta H \cdot g \cdot s + B_2^{\circ} O_2^{\circ} + B_4^{\circ} O_4^{\circ} + B_4^{3} O_4^{3} + B_4^{*3} O_4^{*3}$$

$g_{\parallel} = g_{\perp} = 2.0030$

$B_2^{\circ} = 343.29$ oersteds

$B_4^{\circ} = -0.69102$ oersteds

$|B_4^3| = 15.6$ oersteds

species responsible for this spectrum must consist of more than one atom. The reasoning behind this statement is that the normal sites in calcite have axial symmetry which would predict only two unique g values while this spectrum exhibits three unique g values. These spectroscopic splitting factors are given by $g_{[111]} = 2.0032$, $g_{[11\bar{2}]} = 2.0016$ and $g_{[1\bar{1}0]} = 1.9972$ where we have used the calcite unit cell directions as subscripts to the g values. We also know that, since this must be a molecular species, it must be a molecule or molecule-ion whose ground electronic state is orbitally non-degenerate and furthermore whose first connecting excited state must be far removed from the ground state. This conclusion is drawn from the low anisotropy observed in the g tensor. Fig. 3 gives an isofrequency plot of the "butterscotch" spectrum taken at 77°K with the Zeeman field rotated about the crystal [111]direction. At this temperature the three lines have widths of 0.16 oersteds between points of half intensity.

Our tentative identification of the species responsible for the "butterscotch" spectrum is a CO_2^- ion located at a carbonate ion site. This identification is at present very weak since it requires that a) the explanation be ad hoc and b) the molecule-ion lie in a plane perpendicular to the crystal [111] direction.[23] It further requires that a companion spectrum be observed having an intensity of 5×10^{-3} that of the original due to the one percent abundant carbon-13 isotope whose nuclear spin is 1/2 (see Fig. 4). So far we have not succeeded in observing this doublet hyperfine companion spectrum.

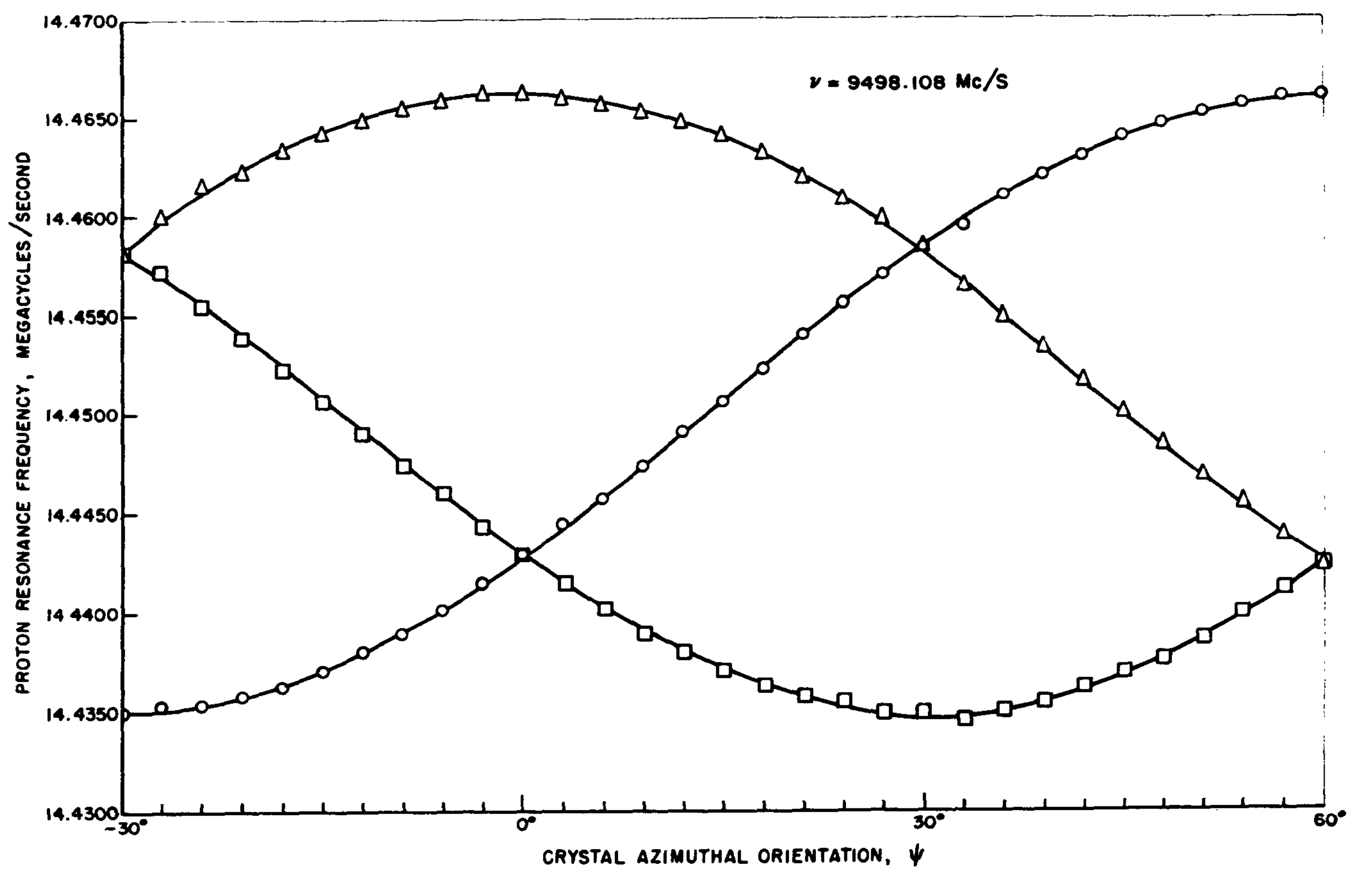


Figure 3. Isofrequency Plot of the Three Line "Butterscotch" Spectrum as a Function of the Azimuthal Angle φ with the Polar Angle $\Theta = 90°$.

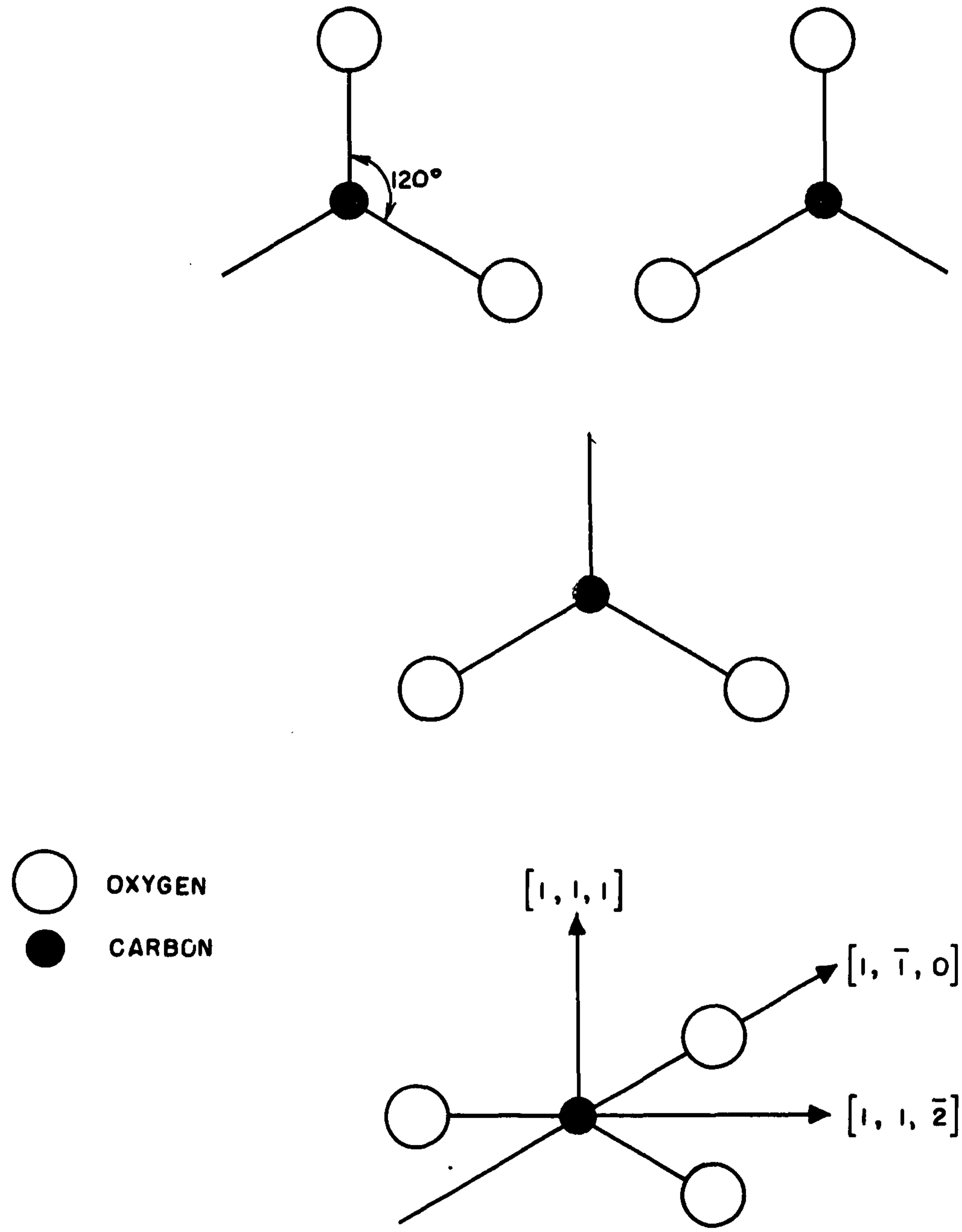


Figure 4. Model of the CO_2^- Molecule Ion Located at a Carbonate Ion Site.

It is probably appropriate at this point to mention briefly our reasons for showing such an interest in the "butterscotch"spectrum. The argument simply has to do with the fact that once the source of this spectrum has been identified we can eliminate it as being responsible for the irradiation-produced five line spectrum. It is our intention to continue the study of this spectrum on the future extension of this contract until we have established a reasonable argument for the identity of the molecular species responsible for this spectrum.

Finally, we have observed a spectrum of four paramagnetic resonance lines which are found to be identical to four of the five lines observed in the irradiated calcite. The four lines observed in the unirradiated calcite are of greatly reduced intensity. The unobserved fifth line corresponds to the central isotropic line of the irradiated calcite. This in itself is quite interesting because of the five resonance absorption lines, the central component is narrowest and most intense meaning that its presence would be easiest to detect. It has been shown beyond any doubt that no one defect center could be responsible for the five line spectrum. This has in effect been an experiment in differential line intensity growth. The spectrum has now been reduced in complexity from five lines to no more than four lines plus the isotropic line. Consider now the four line spectrum. These can, in principle, be due to a state of spin 2 split into two doublets and one singlet. The center, however, cannot occur at a calcium ion site as a spin 2 center would exhibit a splitting of the resonance absorption lines for $\Theta \neq 0$ where Θ is the angle between the magnetic field direction and the crystal C axis. The observed defect lines do not possess this character. Because of the axial symmetry of the spectrum if it is to be located in a carbonate ion site it must either be an ionic state of some atom or an axially symmetric molecule which lies along the [111] direction. With respect to nearest neighbor Ca^{++} ions there is only one type of CO_3^{--} site. However, the next nearest neighbors will again produce two unequivalent sites so that a splitting would again be produced. In addition, molecular species with spin 2 are not very common. From this qualitative argument we may tentatively conclude that the four line spectrum is probably not due to a single center S = 2. The next simplification suggested is that three of the four lines are due to one center of spin S = 3/2. This state would not show a splitting due to the different cubic field axes of the two unequivalent sites. The energy level structure for a spin 3/2 ion in an axial field is easily visualised. At $\Theta = 0°$ it will consist of two doublets separated by an energy which we can call 2D. If H_1, H_2, H_3 correspond to the lowest, middle and high field transitions, it is easy to show that $H_2 = \frac{1}{2}(H_3 \pm H_1)$ where the positive sign corresponds to the case $2D < h\nu$, h being the microwave energy. It is readily verified that of the four remaining transitions (we have already eliminated the isotropic line) no three lines will satisfy either of these conditions with reasonable accuracy. We are then finally led to the tentative conclusion that the five line defect structure is due to at least four different centers. Further experiments along this line should provide additional evidence about the minimum number of defect centers responsible for the five line spectrum. Figure 5 gives an isofrequency plot of the five lines in the irradiated calcite.

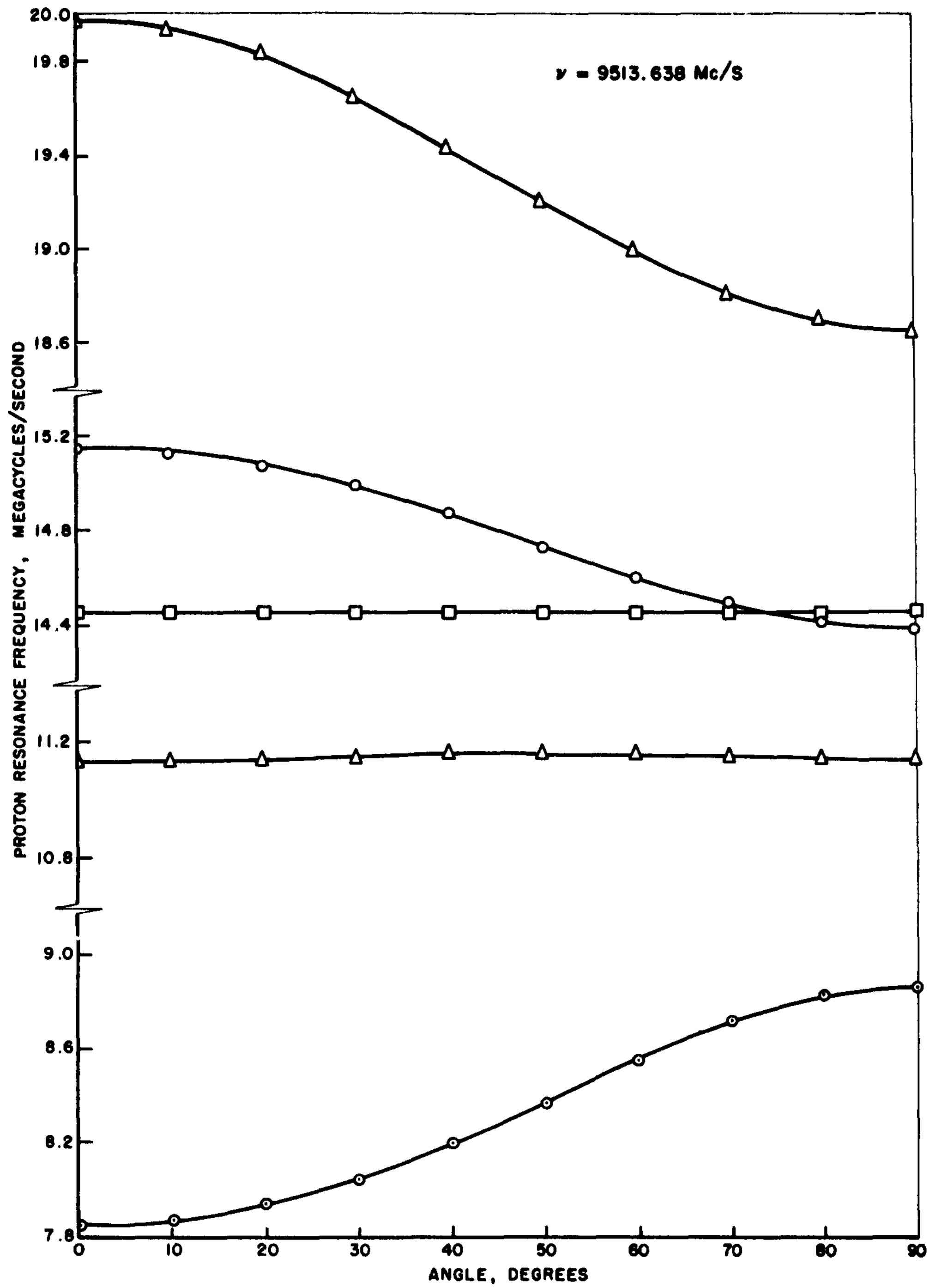


Figure 5. Isofrequency Plot of the Five Lines in Irradiated Calcite Single Crystal

The plot is Zeeman field strength versus the polar axis θ. A similar plot against the azimuthal angle φ provides no variation in the resonance Zeeman field strength. Here is another key piece of information regarding the defect center; that is, whatever the species may be, they must exhibit symmetry about the crystal [111] direction. Table II gives the pertinent information on the five line spectrum for $\Theta = 0°$ and $90°$.

TABLE II
Field positions at ν = 9513.64 Mc/sec for the five lines in x-irradiated single crystal calcite.

Line	$\Theta = 0°$	$\Theta = 90°$	Widths
1	1843.8 oersteds	2083.5 oersteds	0.32 oersteds
2	2609.1 "	2610.2 "	0.37 "
3	3394.7 "	3391.0 "	0.045 "
4	3558.3 "	3377.5 "	0.13 "
5	4691.9 "	4380.2 "	0.35 "

III. SUMMARY

The first phase of the program of studying the irradiation-produced electron paramagnetic resonance absorption spectrum in single crystal calcite can be summarized as follows: a thorough mapping has been performed of the optical and magnetic spectra of unirradiated and irradiated clear and "butterscotch" calcite single crystals. A slight difference has been found in the optical spectra of the irradiated and unirradiated calcite. A study to determine the mechanisms responsible for the different spectra will be undertaken in the next phase of the program. A study will also be pursued to try to understand this difference so as to be able to establish a presence or lack of correlation between the irradiation-produced spectra and the "butterscotch" calcite spectrum.

In the electron paramagnetic resonance absorption spectrum of unirradiated clear and "butterscotch" calcite there has been found no less than 120 lines in the region of zero to 10,000 oersted for x-band spectrometer operation. Of this 120 line spectrum we have identified 30 lines due to divalent manganese, 5 lines due to trivalent iron, 3 lines which are tentatively called the "butterscotch" spectrum and 4 lines which are identified with four or the five irradiation-produced lines. In irradiated calcite a five line spectrum is observed which is noted to exhibit axial symmetry; that is, it shows no dependence on the azimuthal angle φ . Since the characteristics of this spectrum were thoroughly described in our proposal for the initial phase of the program they will be mentioned here only briefly. What has been learned in the interim is that this five line spectrum cannot be adequately described by a single paramagnetic defect center since the central line is not observed in the unirradiated calcite single crystal.

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